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54 **Aqueous composition for the passivation of zinc and cadmium surfaces.**

57 An aqueous composition, fundamentally consisting of organic polymers and chromate ions for the passivation of zinc and cadmium surfaces. These are provided with a high anticorrosive resistance and the traditional colouring of conventional chromate passivation. This immersion process (self colour) does not require subsequent rinsing, thus avoiding production of chromate polluted waste effluent.

EP 0 264 472 A1

"AQUEOUS COMPOSITION FOR THE PASSIVATION OF ZINC AND CADMIUM SURFACES".

The passivation is a method to protect metal against corrosion in mild mediums. The passivation can be obtained in different ways, among them the chemical ones, with the formation of a surface film of metal oxide, for instance chromate plating. The passive state must not be considered as a state in which there is no corrosion, but that one in which the reaction is inhibited by a passive film controlling the diffusion speed with a very low density of dissolution current, of about 10 A per cm².

There are many iron or steel parts being protected superficially against atmospheric pollution. Zinc is the protection metal most currently used, but cadmium is as well largely used. However these metals have a high tendency to corrosion in industrial atmospheres as well as in urban and marine ones.

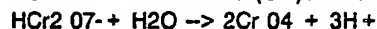
The normal reduction potentials for the pair Zn^{++} / Zn - 0,763 v. compared to the pair Fe^{++} / Fe - 0,44 v. , show that the metal zinc will act as a protection metal when coating steel parts. First observation of normal reduction potentials of the pair Cd^{++} / Cd - 0,403 v. and of the pair Fe^{++} / Fe - 0,440 V, shows that cadmium is more noble than iron. This is due to the fact that iron suffers anodic polarizations, and cadmium does not. The cathodic behaviour is very similar, so that the cadmium which is corroding is anodic with regard to iron, protecting it superficially. Because of the rustability of zinc in the atmosphere, it corrodes giving a voluminous white rust film, with a very disagreeable aspect.

To solve these problems, the most frequent practice is to passivate the iron or the zinc plated steel. This passivation is in fact the chemical absorption of proper corrosion inhibitors, which reduce the corrosion speed of the corroding medium. The passivation implies the stabilization of the species absorbed chemically maintaining a protective film during a certain period of time. These corrosion inhibitors can be: metallic oxide and corrosion products, organic products, and others,

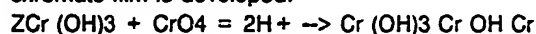
The chromium plating is the most usual passivation procedure onto metal zinc and cadmium surfaces. Presently, a typical chromium plating is composed by solutions of 50 to 200 grs/l of Na₂Cr₂O₇ and 3 to 6 ml of H₂SO₄, this producing a greenish-brown film after about ten seconds of dipping, the optimum application pH of these solutions is between 1'2 and 1'6, and the procedure comprehends three phases:

a) Zinc is dissolved by dynamic acid, increasing then the pH near the surface :
 $Zn + 2H^+ + Cr_2O_7^{2-} \rightarrow Zn^{2+} + 2H_2O + 2Cr^{3+}$

b) The pH increase causes the precipitation of hydroxide, after the reduction of Cr⁺⁶ to Cr⁺³ by hydrogen.



c) Onto metal surface a basic chromium chromate film is developed:



The attack onto zinc surface is quite strong, so that very thin zinc surfaces cannot be chromium plated. This procedure explains the fact that there is no zinc oxide onto surface, but however the precipitate can be very hydrated. This hydrotation loss can comprehend the loss of inhibiting properties, what can be observed with a strong heatening of chromium plated surfaces. Because of the interest of obtaining a decorative finishing, different products have been developed to give chromium platings of different coloration, yellow, black, green, blue and others.

The above described passivations, have been performed in the practice during a long period of time. Presently, there is a trend to protect the chromium plated or passivated surfaces with an organic film.

This is due to the need of increasing the anticorrosive properties, above all in industrial atmospheres with high SO₂ content. On the other hand, to add an organic film onto the chromium plating, protects areas that for a reason or another have not been conveniently passivated. For instance, areas with holes and cavities, where there is a very low zinc electroplating penetration.

Different passivation procedures with organic products have been developed, leaving a protective film onto the zinc chromates. All them comprehend a polymer which remains dissolved or dispersed in a preferently aqueous medium, which can reticulate with an ambient drying or a hot air one. The nature of these polymers is very large from alkyd, polyester, acrylic resins and others. They can content or not polyvalued cations helping in the polymer reticulation process.

In short, the protection process for zinc or cadmium plated surfaces, would comprehend a chromating bath, dipping the pieces to treat in periods from 5 to 10 seconds, to 2 or 3 minutes. Afterwards there would be a cold or hot water rinsing, depending on the process, and an immersion in a protective organic product. A correct squeezing and afterwards a room temperature drying, or a hot air one.

The purpose of present invention is to develop a product with at the same time a chromium plating of zinc or cadmium surface, as well as laying an organic polymer. With this composition, organo-inorganic films are obtained, with a high anticorrosive protection and a decorative finishing similar to the above described traditional passivations.

The product developed in present invention, applied by rack or drum processes, provides a corrosion protective film onto zinc (or cadmium) plated surfaces, with a decorative finishing in different colours, as per the final composition employed. Different finishings can be obtained : blueish-white, olive-green, iridescent yellow, and black.

The application process is extremely simple as the chemical conversion and the polymer laying are performed in the same single bath, not requiring further rinsings.

The process can be schematized as follows :

- Zinc plating.
- Rinsing.
- Bright dipping.
- Rinsing.
- Conversion + Polymer.
- Drying.

The basic operation principle of this invention consists in a simultaneous action of the different elements of the composition to form a mixed insoluble film of chromates and polymers, of high anticorrosive resistance and a decorative colour as above described.

The different elements of this invention (the function of which is described further on) act as follows : the existing mineral acids attack the zinc surface with formation of ions of Zn^{++} and H^{+} . These rising ions will provoke a reduction of existing hexavalent chromium, with a change in the pH value in the interface of the polymer next to the metal surface with the subsequent unstabilization, coagulation and unsolubilization of the polymer. Afterwards, the polymer reticulates with the metallic polyvalent ions present, performing a "closed" film highly resistant to corrosion.

A characteristic of this procedure is the fact that the treatment time can modify and control the thickness of the coating obtained, the protective film being thicker when treatment time is longer, so that some limits have been fixed to make possible the industrial application of this process, which are scheduled between 20 seconds and 120 seconds of treatment time. Working under these conditions, films with thicknesses of 0,5 up to 2 microns, can be obtained, corresponding to a weight of 0,75 to 3 grs/m².

The advantages of the passivation procedure using above described product, can be classified as follows :

Operation - besides the simplicity of the process we have already described, it is obvious that the elimination of the rinsing step, indispensable in the traditional processes, implies an important saving in water and space. On the other hand, there is a reduction in the quantity of waste waters to decontaminate.

Anticorrosion - The high anticorrosive protection reached is explained by the high weight of coat laid by the product of this invention, and also by the structure itself of the coating, which because of being highly reticulated, presents a surface with a poor porosity, with an effective isolation of the corrosion circuit between anode and cathode.

As an example, we will indicate that an iridescent-yellow coating, with a layer weight of about 1 to 1,7 gr/m², can protect from corrosion up to 250-300 hours as per Salt Spray ASTM-B-117, up to white rust.

A blueish-white coating, with layer thickness of 1 gr/m², has a resistance of 100 to 125 hours.

A black coating, of 2,5 to 2,8 gr/m², resists from 350 to 400 hours, and a olive-green coating of 2,2 to 2,6 gr/m² can reach up to 500 hours.

The resistance in industrial atmospheres is also remarkable, as per the Kesternich test, standard DIN 50018-2S, in which coatings of 2 to 3 gr/m² can resist from 4 to 5 cycles.

Other details and features of present Patent will be developed further on. These details are given by the way of examples, making reference to a possible case in the practice, but not limited to these very details ; therefore this description must be considered from an illustrative point of view and without any limit.

As already explained, the function of every component can be synthetized as follows :

The Cr VI Salts, which will be in the system shaped as soluble anions, will give under a reduction process chromium ions (III). As well, the Cr VI Salts will give the anions which will precipitate with the present cations, which are solved or formed, as per the different solubility of every chromate or dichromate. Therefore there will be a precipitate of inorganic salts onto the zinc plated surface dipped in the system.

The mineral acids, which will attack the zinc or cadmium plated surface, solving in the medium Zn^{++} or Cd^{++} ions, forming at the same time hydrogen which will provoke the reduction of the Cr VI salts to Cr^{++} ions. As well, these acids will give to the system a low pH, preventing the precipitation of the hydroxides of the different cations present in the system. The anions derivated from these acids will also enter in the precipitated film, forming slats with the adequate precipitating cation.

The inorganic Salts which provide the system with cations and anions, which will form salts with the cations being solubilized, which in their turn precipitate by supersaturation or by coprecipitation onto the zinc or cadmium plated surface. The colours of the film laid, will above all depend of the choice of these inorganic salts.

The organic polymers precipitating or coprecipitating in the interface next to the zinc plated surface, due to sharp variations of the ionic force or of the pH of the system in this interface. These polymers will form together with the inorganic precipitates a tridimensionally reticulated system, so that the laid film will have a high anticorrosive protection.

In order that this passivation procedure could be developed in the steps of zinc plating, rinsing, bright dipping, rinsing, conversion plus polymer and drying, the product to use will comprehend :

Organic component of the system, henceforth named component "A". The organic product being the base of the formation of a polymeric film onto the treated part, will enter in the final product in an aqueous dispersion shape. The resin produced by the system of polymerisation in emulsion will contain polymers of acids and esters such as acrylic, metacrylic, ethyl-acrylate, butyl-acrylate, and other monomers like styrene. Thus, we obtain a dispersion with particles of a medium size of 0,1 microns, the product having a density of 1,04 to 1,06 gr/cc.

An important part of component "A" is the incorporation, by means of the procedure of emulsion inside the polymerisation, or by further incorporation to the system, of other polymers of low molecular weight, giving to the surface of dry organic film, lubricating properties. Thus, pieces (specially screws and nuts), treated by the process described, have self-lubricating properties, preventing the use of a further oiling with the corresponding saving in manpower and treating time. The inorganic fraction of the system, that is the one producing a first attack to zinc, and the formation of chromates and insoluble salts, will be named henceforth component "B". It is evident that chemical composition of component "B" will vary in some of its ingredients depending of the colour of the passivate finishing to obtain, although always maintaining the hexavalent chromium as a common and main element.

The choice of products entering in component "B" comprehends 3 basic groups, forming the conversion layer onto the zinc surface. Composition: hexavalent chromium, occasionally trivalent, like chromates, dichromates, chromium dioxide, chromium +3 salts ; strong mineral acids, to start the attack, like sulfuric acid, nitric acid, fluorhydric, acid fluorures. They will also maintain the control of the pH value of the product. Occasionally, will be nec-

essary the participation of some inorganic cations, the salts or insoluble acids of which formed during the process of attack to zinc, will give a coloration to the chromate layer. We can use cations such as in Cu, Ag, Cr+3, and others such as sulphates, acetates, nitrates, borates. This selection of elements will be incorporated or not inside component "B", and if not it will be named component "C".

Some examples of components of the inorganic fraction of component "B" will be as follows :

1st example. Chromic acid - 5 to 20%

Amonic sulfate - 1 to 4%

Mineral acid - 2 to 7%

Distilled water - up to 100 gr.

2nd example. Chromic acid - 5 to 20%

Amonic sulfate - 0,2 to 2%

Ammonia 25% - 5 to 10%

Distilled water - up to 100 gr.

3rd example. Chromic acid - 1 to 4%

Amonic sulfate - 0,2 to 2%

Sodic fluorure - 2 to 6%

Mineral acid - 0,2 to 3%

Distilled water - 0,2 to 3%

4th example. Chromic acid - 12 to 30%

Amonic sulfate - 4 to 10%

Mineral acid - 2 to 6%

Distilled water - up to 100 gr.

The bath formation to obtain a chromate-polymer coating, object of the procedure of passivation will be made as follows :

Example A, to obtain a olive green coating, of above mentioned qualities
component "A" - as per above description - 75 to 120 cc.

component "B" - as per first example - 75 to 120 cc.

Distilled water - up to 1000 cc.

Example B, for a yellow iridescent coating, with above mentioned qualities

component "A" - as per above description - 50 to 100 cc.

component "B" - as per second example - 50 to 100 cc.

Distilled water - up to 1000 cc.

Example C, to obtain a blueish-white coating, with above mentioned qualities

component "A" - as per former description - 50 to 100 cc.

Component "B" - as per third example - 75 to 100 cc.

Distilled water - up to 1000 cc.

Example D, to obtain a black coating, of above mentioned qualities

component "A" - as per above description - 80 to 120 cc.

component "B" - as per fourth example - 70 to 100 cc.

component "C" - as per above description -
distilled water - up to 1000 cc.

Having sufficiently described the contents of present patent, it is understood that there is the possibility of introducing in it any modification of detail which would be estimated to be necessary, if not changing the essence of the Patent, which is resumed in following VINDICATIONS :

Claims

1st - "AQUEOUS COMPOSITION FOR THE PASSIVATION OF ZINC AND CADMIUM SURFACES", characterized by containing inorganic acids and organic polymers that are applied by dipping in a sole bath, not needing any rinsing after its application.

2nd - "AQUEOUS COMPOSITION FOR THE PASSIVATION OF ZINC AND CADMIUM SURFACES", characterized as per former VINDICATION, by the fact of containing organic polymers in dispersions as described in the text as component "A".

3rd - "AQUEOUS COMPOSITION FOR THE PASSIVATION OF ZINC AND CADMIUM SURFACES", characterized because of the fact that the composition of named component "A" includes polymers of low molecular weight with lubricating character.

4th - "AQUEOUS COMPOSITION FOR THE PASSIVATION OF ZINC AND CADMIUM SURFACES", characterized as per first VINDICATION, because the composition contains mineral acids, anions and cations such as described in the text as component "B".

5th - "AQUEOUS COMPOSITION FOR THE PASSIVATION OF ZINC AND CADMIUM SURFACES", characterized because the composition of component "B", is as per example no. 1.

8th - "AQUEOUS COMPOSITION FOR THE PASSIVATION OF ZINC AND CADMIUM SURFACES", characterized because the composition of component "B", is as per example no. 2.

7th - "AQUEOUS COMPOSITION FOR THE PASSIVATION OF ZINC AND CADMIUM SURFACES", characterized because the composition of mentioned component "B", is as per example no.3.

8th - "AQUEOUS COMPOSITION FOR THE PASSIVATION OF ZINC AND CADMIUM SURFACES", characterized because the composition of mentioned component "B", is as per example no.4.

9th - "AQUEOUS COMPOSITION FOR THE PASSIVATION OF ZINC AND CADMIUM SURFACES", characterized as per first VINDICATION,

because the composition of the dipping treating bath is formed with components "A" and "B", as per examples A, B, and C.

10th - "AQUEOUS COMPOSITION FOR THE PASSIVATION OF ZINC AND CADMIUM SURFACES", characterized as per VINDICATION 1st and 4th, because the composition of the dipping treating bath is formed with components A, B, C, as per example D.

11th - "AQUEOUS COMPOSITION FOR THE PASSIVATION OF ZINC AND CADMIUM SURFACES", characterized as per THE VINDICATION, because the composition of named component "C" is the one described in the text.



EP 86 11 4575

| DOCUMENTS CONSIDERED TO BE RELEVANT | | | |
|---|---|--|--|
| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim | CLASSIFICATION OF THE APPLICATION (Int. Cl. 4) |
| X | DE-A-3 407 283 (ELEKTRO-BRITE GmbH) * Claims 1-6 * | 1-9 | C 23 C 22/28 |
| X | FR-A-1 295 687 (YAWATA IRON & STEEL) * Abstract, points 1,2 * | 1-11 | |
| X | FR-A-1 154 580 (SOCIETE CONTINENTALE PARKER) * Abstract, points 1a, 1e, 2a, 2f, 2g; page 8, example 11 * | 1-3, 10, 11 | |
| A | EP-A-0 087 288 (M & T CHEMICALS) * Claims 1,5; page 1, line 1 - page 2, line 15 * | 1,4-11 | |
| A | FR-A-1 255 706 (SOCIETE CONTINENTALE PARKER) * Abstract, points 1,7 * | 1,4-6, 8-11 | C 23 C 22/00 |
| The present search report has been drawn up for all claims | | | |
| Place of search THE HAGUE | | Date of completion of the search 18-06-1987 | Examiner TORES F.M.G. |
| CATEGORY OF CITED DOCUMENTS | | | |
| X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document | | T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons A : member of the same patent family, corresponding document | |